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(54) Title: POLYPROPYLENE COMPOSITION AND METHOD FOR FUNCTIONALIZATION OF POLYPROPYLENE

(57) Abstract

The present invention relates to a process for the functionalization, and preferably the maleation of a polyolefin, preferably polypropylene, by use of a selected class of peroxides which will not cause the molecular weight of the polyolefin to significantly degrade. The class of peroxide initiators which are capable of successful use in the present invention may be more broadly classified as peroxides which have radical fragments when the peroxide is dissociated, which are a combination of R. and RO., where R is an aliphatic hydrocarbon, and O is oxygen. The preferred peroxide initiators for use in carrying out the present invention so as to obtain the results indicated above are t-butyl peroxypivalate and isononanoyl peroxide. The composition resulting from the practice of the process of the invention is a maleated polypropylene in which the polypropylene has more than 0.3 weight percent grafted maleic anhydride and preferably greater than 0.4 weight percent, for example, from 0.4 to 4 weight percent or more grafted maleic anhydride on the polymer chains and in which the MFR is less than 100.

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POLYPROPYLENE COMPOSITION AND METHOD FOR FUNCTIONALIZATION
OF POLYPROPYLENE

1   This invention relates to a new functionalized polypropylene

2   composition and a new and improved process for the

3   functionalization of polypropylene, particularly the maleation of

4   polypropylene.

5   Brief Description of the Prior Art

6   To prepare polypropylene for certain end-use applications it

7   is necessary to functionalize the polymer, i.e., to incorporate

8   functional groups such as maleic anhydride onto the polypropylene

9   polymer chains. The reaction of maleic anhydride with

10   polypropylene is well known in the art. Examples of the prior art

11   are U.S. Patent Nos. 4,404,312; 4,506,056; 3,414,551; 4,370,450;

12   and 4,639,495. European Patent application O 225 186 is another

13   example of a method of grafting maleic anhydride onto

14   polypropylene. In the prior art, the maleation of polypropylene

15   has been accomplished by the use of free radical initiators such

16   as a peroxide initiator to induce maleation. However, the prior

17   art peroxides which have been used for functionalizing

18   polypropylene cause substantial degradation of the molecular

19   weight of the maleated polypropylene. In an attempt to avoid

20   molecular weight degradation of the maleated polypropylene the

21   prior art methods employed low levels of peroxide initiator. See,

22   for example, U.S. Patent No. 4,404,312 which states that the

23   organic peroxide should not be more than about 0.1 percent by

24   weight, and preferably not more than 0.01 percent by weight of the

25   polypropylene to be reacted. As a result, in the prior art, the

26   extent of maleation of the polypropylene has been restricted.

27   Other attempts to avoid the molecular weight degradation require

28   the use of a third ingredient, such as styrene, which becomes a

29   part of the polymer, or require the use of a catalyst such as

30   N,N-dialkylethanolamine, or other nitrogen, phosphorus, or sulfur

1   containing compounds. Examples of such ingredients are found in
2   U.S. Patent No. 4,506,056 and EPO Application O 225 186.
3   <u>Summary of the Invention</u>
4   The present invention is a novel composition wherein the
5   molecular weight of a functionalized polypropylene product is
6   greater than heretofore obtained with the prior art radical
7   initiators, and a novel functionalization process wherein minimal
8   molecular weight degradation of the polypropylene occurs during a
9   radical initiated functionalization process. This is accomplished
10   by the use of a selected class of peroxides which have been found
11   to produce significant grafting of unsaturated monomers useful for
12   functionalizing polypropylene, such as maleic anhydride, himic
13   anhydride, acrylic acid, methacrylic acid, vinyltrimethoxysilane,
14   acrylamide, itaconic acid, maleic acid, fumaric acid, monomethyl
15   maleate, monoethyl maleate, fumaric anhydride, vinyl amines and
16   amides, and other substituted vinyl monomers that are capable of
17   free radical polymerization, onto polypropylene without causing
18   significant molecular weight degradation of the polypropylene.
19   Polypropylene has many attractive characteristics such as a
20   high melting temperature, low density, chemical inertness and low
21   cost. However, in order to use polypropylene in applications such
22   as adhesives, coextrudable tie layers for multilayer composites,
23   metal coatings, and polymer blends, it is necessary to chemically
24   modify polypropylene to incorporate a reactive moiety onto the
25   backbone of the polymer. As a primary advantage of the present
26   invention, one can employ high levels of peroxide and obtain a
27   polymer composition having a high molecular weight with a
28   significant level of functionality which can be made into film or
29   otherwise processed by extrusion, fiber spinning, etc. In
30   contrast, the lower molecular weight functionalized polypropylene
31   produced by conventional approaches generally cannot be so used or
32   processed.
33   A further advantage of the present invention is that the
34   molecular weight degradation of polypropylene can be controlled,
35   independent of the level of grafting of maleic anhydride onto the
36   polypropylene, through variation in temperature, time and other
37   process variables. In the prior art, molecular weight degradation

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1   increases when increasing amounts of peroxides are used to
2   increase grafting.
3   The process of this invention does not require the presence of
4   a catalyst, additive, or process modifier (third ingredient) as
5   disclosed in U.S. 4,506,056 to prevent molecular weight
6   degradation. The functionalized polypropylene compounds produced
7   with the process of this invention have a melt flow rate (MFR) of
8   one hundred (100) or less, (measured by ASTM Standard F 1238-86),
9   but preferably seventy-five (75) or less. The peroxide initiators
10 preferred for use in practice of the process have a short
11 half-life $(t_{1/2})$ at 180°C, preferably less than 3 seconds at
12 180°C, and the peroxide initiator decomposes to produce radical
13 fragments in combinations of either R• or RO•, wherein R is an
14 alkyl group, preferably a C_1-C_{30} alkyl group. When the
15 radical is RO•, R is most preferably t-butyl. The energy for
16 bonding a hydrogen atom to these types of radicals is about 105
17 Kcal/mol or less. The peroxides preferred for use in the process
18 are t-butyl peroxypivalate or isononanoyl peroxide.
19 Brief Description of the Drawings
20   Figure 1 is a graph of the melt flow rate (MFR) versus the
21 weight percent of maleic anhydride incorporated for maleated
22 polypropylene compositions produced by using dicumyl peroxide, a
23 typical peroxide used in radical initiated grafting processes,
24 compared to a maleated polypropylene composition produced by
25 either of two preferred embodiments of the process of the present
26 invention, one embodiment being a melt phase process (B) and the
27 second embodiment being a solid phase process (C).
28   Figure 2 is a graph of the melt flow rate (MFR) of a
29 functionalized polypropylene versus the amount of peroxide
30 initiator used to produce the functionalized polypropylene
31 composition, for a functionalized polypropylene produced using
32 dicumyl peroxide in accordance with prior art processes (D) and
33 for a functionalized polypropylene produced using t-butyl
34 peroxypivalate in accordance with the process of this invention
35 (E).
36 Detailed Description of the Invention
37   The present invention relates to a process for the

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1 functionalization, and preferably the maleation of a polyolefin,
2 preferably polypropylene, by use of a selected class of peroxides
3 which will not cause the molecular weight of the polyolefin to
4 significantly degrade. While the differences between
5 polypropylene and its copolymers are recognized, the term
6 "polypropylene" as used in the claims includes both homopolymers
7 and copolymers of propylene for the sake of convenience. The
8 process of this invention does not require the presence of a
9 catalyst, additive, or process modifier to prevent molecular
10 weight degradation.
11   The functionalizing agent employed in the process of this
12 invention may be any of the unsaturated monomers conventionally
13 used to functionalize a polyolefin. Such functionalizing agents
14 include, for example, carboxylic acids such as acrylic and
15 methacrylic acid; acid anhydrides such as maleic and himic
16 anhydride; acid amides such as acrylamide; and vinyl siloxanes
17 such as vinyltrimethoxysilane. The functionalizing agent
18 preferred for use in the process shall be described and
19 illustrated with reference to the functionalization of
20 polypropylene by reaction with maleic anhydride (MAH). Although
21 the invention will be described with reference to maleic
22 anhydride, it should be understood that functionalizing reagents
23 different from maleic anhydride, such as the unsaturated monomers
24 previously identified, can be employed in the practice of this
25 invention. Accordingly, the term "maleation" or "maleated" as
26 used hereafter should be understood to mean "functionalization"
27 insofar as the use of functionalizing reagents other than maleic
28 anhydride are contemplated for use in the process of the invention.
29   The composition resulting from the practice of the process of
30 the invention is a maleated polypropylene in which the
31 polypropylene has on the average more than 0.3 weight percent
32 (0.13 mole %) grafted maleic anhydride and preferably greater than
33 0.4 weight percent (0.17 mole %) grafted maleic anhydride, and an
34 MFR of less than 100. The mole % most preferably is in the range
35 of 0.13-1.71.
36   The melt flow rate (MFR) of the maleated polypropylene,
37 measured by ASTM Standard E1238-8, is about one hundred (100) or

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1   less, preferably less than 75, and most preferably less than 60.
2   These values can be compared with the prior art as in Table 2
3   where it is demonstrated that the use of peroxides typically used
4   in the prior art produces maleated polypropylenes with MFR's
5   greater than 300. Maleated polypropylene made by the prior art
6   methods with an MFR of less than 100 contain very low levels of
7   grafted maleic anhydride, as demonstrated by the overlapping area
8   of the curves in Figure 1 in the region of very low weight percent
9   grafted maleic anhydride, low MFR. In accordance with this
10 invention in which polypropylene does not significantly degrade,
11 the MFR of the maleated polypropylene product is related to the
12 MFR of the initial polypropylene polymer. The advantage of the
13 composition of this invention is that the maleated polymer product
14 can be made into films or can be processed by extrusion, fiber
15 spinning, etc., and used in engineering plastic applications
16 whereas the lower molecular weight functionalized polymers
17 produced by prior art functionalization processes generally have
18 MFR's much greater than 100 and cannot be so processed.
19   In carrying out the process of the present invention, the
20 maleic anhydride and peroxide reagents should be mixed with the
21 polypropylene preferably before the polypropylene is heated, and
22 most preferably the maleic anhydride and the peroxide free radical
23 initiator should be mixed prior to adding such mixture to the
24 polypropylene. Although use of a solvent is not required for
25 mixing the reagents with polypropylene, using an inert, low
26 molecular weight, volatile solvent, such as pentane, hexane, or
27 other hydrocarbons, or methylethyl ketone, acetone, or other low
28 molecular weight species, or any other suitable liquid, to coat
29 the polymer with the reagents, does improve the mixing of the
30 reagents and improve the dispersion of the reagent mixture on the
31 polypropylene when so used. The mixture of peroxide initiator and
32 maleic anhydride is added to the polypropylene to coat the polymer
33 with such components of the mixture. If a solvent is used as a
34 coating and dispersion aid for the reagents, after the mixture is
35 coated onto the polypropylene the solvent is evaporated from the
36 polymer, leaving the maleic anhydride and peroxide reagents on the
37 surface of the polypropylene.

1   Thereafter, the polymer with the reagents present is treated
2   in one of two ways.
3   A preferred mode for conducting the reaction of maleic
4   anhydride with polypropylene is in the melt phase mode wherein the
5   temperature exceeds 160°C. In accordance with this embodiment, a
6   high level of grafting with minimal molecular weight degradation
7   is obtained. In accordance with this mode, the polypropylene is
8   mixed with the peroxide and maleic anhydride or coated by
9   evaporation of inert diluent from a slurry of peroxide/maleic
10   anhydride. Typical diluents are pentane, heptane, methyl, ethyl,
11   ketone and the like. Thereafter, the reagent coated polypropylene
12   granules or pellets are heated in a vessel such as a Brabender
13   plasticorder, an autoclave, an extruder or other equipment of like
14   purpose or are reacted in a fluidized bed or gas phase reactor.
15   Good results are obtained at temperatures of about 180-250°C, but
16   preferably 180-220°C. The longer the time that the polypropylene
17   is subjected to the reaction temperature, namely the preferred
18   temperature of 180-220°C, the greater will be the amount of
19   grafted maleic anhydride, without further degrading the molecular
20   weight of the polypropylene.
21   An alternative method for conducting the maleation reaction is
22   in the particulate or solid phase, at a temperature below the
23   melting point of the polypropylene, namely at a temperature of
24   less than about 165°C. In accordance with this mode, the closer
25   to 165°C the better the grafting results obtained. The MFR of
26   maleated polypropylene products produced in the particulate phase
27   is less than fifty (50) but most commonly less than ten (10) when
28   starting with a polypropylene resin having an MFR of 3. The
29   longer the time that the polypropylene is subjected to the
30   reaction temperature, namely the preferred temperature of
31   150-165°C, the greater will be the amount of the grafted maleic
32   anhydride, without further degrading the molecular weight of the
33   polypropylene.
34   Alternatively, in either the melt phase or solid phase mode,
35   the maleic anhydride and the select peroxide can be added to the
36   polypropylene separately. Addition of the maleic anhydride
37   separately from the peroxide results in lower grafting levels, but

1   maintains the advantage of insignificant molecular weight
2   degradation of the polymer product.
3   Since in the process of the present invention the molecular
4   weight of the polypropylene is not significantly degraded, the
5   amount of the peroxide used, based on the quantity of
6   polypropylene to be reacted, may be as high as 10 mole percent,
7   calculated as the number of moles of peroxide per mole of
8   propylene monomer units (C_3H_6 units) present. The preferred
9   amounts of the peroxide initiator are in the range of about 0.14
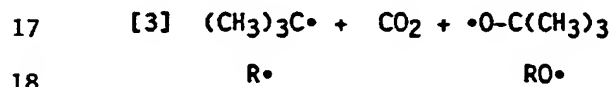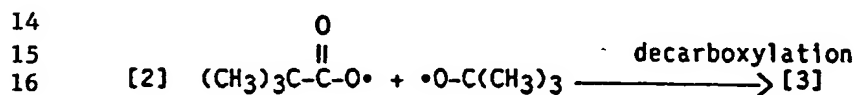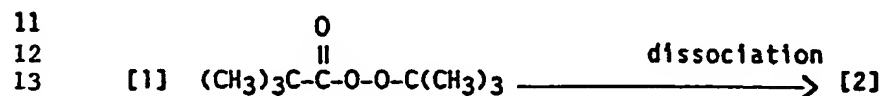10 to 6 mole percent.
11   The presence of a catalyst, additive, or other process
12 modifier during reaction is not required in order to accomplish
13 the objectives of the present invention, namely, the grafting of
14 substantial quantities of maleic anhydride to polypropylene
15 without significant degradation of the polypropylene molecular
16 weight. However, such catalysts, additives, or other process
17 modifiers can be included in this reaction to obtain similar
18 results as given in the prior art for other processes using other
19 peroxides (EPO Patent Application 0 225 186). As above mentioned,
20 it is generally desirable in this invention to use a minor amount
21 of a low molecular weight hydrocarbon or other solvent to enhance
22 the mixing of the reagents and to disperse the reagent mixture on
23 the polypropylene.
24   With the process of the present invention the maleated
25 polypropylene produced will have an MFR of one hundred (100) or
26 less, i.e., from 0 to 100, and desirably 0-75, and most desirably
27 0-60, indicating that the molecular weight of the maleated
28 polypropylene product is much higher than the prior art polymers
29 of polypropylene with equivalent amounts of maleic anhyoride
30 grafted using peroxide initiators. Also, in accordance with this
31 invention the amount of maleic anhydride grafted is greater than
32 0.3 weight percent and preferably greater than 0.4 weight percent
33 grafted maleic anhydride with an MFR of less than 100 which
34 distinguishes the present invention from the prior art.
35   The preferred peroxide initiators for use in carrying out the
36 present invention so as to obtain the results indicated above are
37 t-butyl peroxypivalate and isononanoyl peroxide. The class of

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1   peroxide initiators which are capable of successful use in the
2   present invention may be more broadly classified as peroxides
3   which have radical fragments when the peroxide is dissociated,
4   which are a combination of R• and RO•, where R is an aliphatic
5   hydrocarbon, and O is oxygen. Such radical fragments exist (1)
6   when the peroxide separates at the two oxygen atoms in the middle
7   of the peroxide (dissociation), or (2) when the fragments formed
8   by dissociation undergo decarboxylation or beta-scission after
9   separation at the two oxygen atoms in the middle of the peroxide.
10 The dissociation pathway for t-butyl peroxypivalate is:

11   O
12 || dissociation
13   [1]   (CH$_3$)$_3$C-C-O-O-C(CH$_3$)$_3$ ───────────────> [2]

14   O
15 || decarboxylation
16   [2]   (CH$_3$)$_3$C-C-O• + •O-C(CH$_3$)$_3$ ──────────> [3]

17   [3]   (CH$_3$)$_3$C• + CO$_2$ + •O-C(CH$_3$)$_3$

18   R•   RO•

19   It has been found that the hydrogen bond energy, i.e the
20 energy gained by adding a hydrogen radical (H•) to a peroxide
21 radical (P•):

22   P• + H• ------------> P-H   ΔH = hydrogen bond energy

23 can be related to whether the peroxide initiator will function in
24 the present invention. Table 1 shows the hydrogen bond energy and
25 conversely the radical stability for various free radicals or
26 radical fragments which may exist after a peroxide dissociates.

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TABLE 1

Radical Type	Approximate Hydrogen Bond Energy	Radical Reactivity (Hydrogen Abstraction)
⬡• or ⬡–O	112 Kcal/mol	Most Reactive
RO•	105 Kcal/mol	
H_3C•	104 Kcal/mol	
RCH_2•	98 Kcal/mol	
R_2CH•	95 Kcal/mol	
R_3C•	91 Kcal/mol	Least Reactive

Peroxides which dissociate into free radicals with a hydrogen bond energy of about 105 Kcal/mol and below, and which have a short half life at 180°C are most satisfactory for the purposes of the present invention, namely, producing a functionalized polypropylene, particularly a maleated polypropylene, with minimal degradation of its molecular weight.

EXAMPLES

In the examples and tables which follow, the quantities of reagents employed and the properties of resulting compositions were determined as follows:

The melt flow rate (MFR) of the starting polymer and of the maleated polymer product were determined in accordance with ASTM Standard D1238-86, i.e., a melt temperature of 230°C and a load of 2.16 Kg.

The amount of maleic anhydride (MAH) used for reaction with a polymer is reported as weight percent MAH. The weight percent MAH was calculated as the number of grams of maleic anhydride present per gram of polymer multiplied by 100.

The molar concentration of peroxide used, as reported in the

1   examples and tables, was calculated as the number of moles of
2   peroxide per mole of monomer units in the polymer being reacted.
3   Wherein polypropylene was the polymer reacted (Examples 1 to 23)
4   the molar concentration of peroxide used was calculated as the
5   ratio of the moles of peroxide to the moles of propylene monomer
6   units (C_3H_6, M.W. = 42 g/mole) present in the polymer.
7   Wherein an ethylene-propylene copolymer was the polymer reacted
8   (in Examples 23-27) the molar concentration of peroxide used was
9   calculated as the ratio of moles of peroxide to the sum of the
10 moles of propylene and ethylene monomer units (C_3H_6, M.W. = 42
11 g/mole; C_4H_4, M.W. = 28 g/mole) present.

12   To determine the amount of maleic anhydride grafted onto the
13 polymer, the maleated polymer was dissolved in xylene then
14 precipitated from solution with acetone, filtered and dried. All
15 samples in the examples were treated in this fashion. The weight
16 percent of maleic anhydride grafted to the polymer was then
17 determined by Fourier Transform Infrared (FTIR) analysis. FTIR
18 films were pressed at 230°C for several minutes. The maleic
19 anhydride concentrations grafted to the polymer were calculated
20 from the intensity of the peak appearing between 1782-1790 cm^{-1}.
21 The FTIR was calibrated by oxygen analysis performed on maleated
22 polypropylene and maleated ethylene-propylene rubber samples. The
23 molecular weight of the grafted polymer was monitored by measuring
24 the melt flow rate (MFR) using ASTM Standard D1238-86 and by Gel
25 Permeation Chromatography (GPC).

26   The amount of maleic anhydride and peroxide reagents used and
27 their relative concentration, as well as the temperature chosen,
28 the time of reaction, the MFR or molecular weight of the polymer
29 starting material, and the method of addition of the reagents to
30 the polymer starting material were chosen to illustrate the
31 variety of desired results that may be achieved by varying such
32 conditions in the practice of the process of this invention. The
33 examples which follow are illustrative of such variations, but are
34 not intended to limit or otherwise exclude other combinations of
35 such parameters.

36   Specific examples of peroxide initiators which are
37 unsatisfactory and those which are satisfactory in carrying out

1 the present invention are given below as Examples 1-11
2 (comparative) and Examples 12-13 (inventive). Table 2, following
3 Example 13, shows data obtained for the various peroxide
4 initiators utilized in Examples 1-13. Examples labelled with a
5 "C" are comparative examples.

6 Example 1-C

7   The reaction of isotactic polypropylene having a melt flow
8 rate (MFR) of 3.0 and maleic anhydride in the presence of a
9 peroxide initiator was carried out in a Brabender plasticorder.
10 One hundred forty-four milligrams (144 mg) of dicumyl peroxide
11 (0.07 mole percent) was mixed with 1.6 g maleic anhydride (5
12 weight percent) at room temperature in the powder form and then
13 mixed with 32 grams of polypropylene granules. The Brabender
14 plasticorder was brought to a temperature of 180°C and rotated at
15 30 rpm. While rotating at 30 rpm, the powdered peroxide-maleic
16 anhydride-polypropylene mixture was added to the Brabender
17 plasticorder after which the speed of the Brabender was increased
18 to 60 rpm. The polymer mixture was blended for 10 minutes at
19 180°C, then removed from the Brabender. The results are
20 summarized in Table 2.

21 Example 2-C

22   The procedure of Example 1 was followed except that 0.14 mole
23 percent dicumyl peroxide (288) mg was used. The results are
24 summarized in Table 2.

25 Example 3-C

26   The procedure of Example 1 was followed except that 0.24 mole
27 percent dicumyl peroxide (0.48 g) was used. The results are
28 summarized in Table 2.

29 Example 4-C

30   The procedure of Example 1 was followed except that 0.31 mole
31 percent dicumyl peroxide (0.64 g) was used. The results are
32 summarized in Table 2.

33 Example 5-C

34   The procedure of Example 1 was followed except that 0.47 mole
35 percent dicumyl peroxide (0.96 g) was used. The results are
36 summarized in Table 2.

1   Example 6-C
2   The procedure of Example 1 was followed except that 0.62 mole
3   percent dicumyl peroxide (1.3 g) was used. The results are
4   summarized in Table 2.
5   Example 7-C
6   The procedure of Example 1 was followed except that 0.78 mole
7   percent dicumyl peroxide (1.6 g) was used. The results are
8   summarized in Table 2.
9   Example 8-C
10   The procedure of Example 1 was followed except that 4.05 grams
11 of dicumyl peroxide (1.75 mole percent) 3.6 grams of maleic
12 anhydride (10 weight percent MAH) and 36 grams of polypropylene
13 were used. The results are summarized in Table 2.
14 Example 9-C
15   The reaction of isotactic polypropylene having a MFR of 3.0
16 and maleic anhydride in the presence of a peroxide initiator was
17 carried out in a Brabender plasticorder. Maleic anhydride, 10
18 weight percent, and 2,5-dimethyl-2,-5-di(t-butylperoxy) hexane
19 (tradename Lupersol 101), 1.75 mole percent, were dissolved in
20 methyl ethylketone at ambient temperature, then mixed with 36 g
21 polypropylene granules. The solvent was then evaporated from the
22 mixture to leave the peroxide and MAH reagents on the surface of
23 the polypropylene granules. A brabender plasticorder was brought
24 to a temperature of 180°C and rotated at 30 rpm. While rotating
25 at 30 rpm, the peroxide-maleic anhydride-polypropylene mixture was
26 added to the Brabender plasticorder after which the speed of the
27 Brabender was increased to 60 rpm. The polymer mixture was
28 blended for 10 minutes at 180°C, then removed from the Brabender.
29 The results are summarized in Table 2.
30 Example 10-C
31   The procedure of Example 9 was followed except that 1.75 mole
32 percent of t-butyl peracetate (3.6 g) was used as the peroxide
33 initiator. The results are summarized in Table 2.
34 Example 11-C
35   The procedure of Example 9 was followed except that 1.75 mole
36 percent of benzoyl peroxide (3.9 g) was used as the peroxide
37 initiator. The results are summarized in Table 2.

1   Example 12
2   The procedure of Example 9 was followed except that 1.61 mole
3   percent of isononanoyl peroxide (7.2 g) was used as the peroxide
4   initiator and 20 weight percent MAH was used. The polymer mixture
5   was blended for five minutes at 210°C. The results are summarized
6   in Table 2.
7   Example 13
8   The procedure of Example 9 was followed except that 1.75 mole
9   percent of t-butyl peroxypivalate (3.6 g) was used as the peroxide
10 initiator. The results are summarized in Table 2.

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Table 2.

EXP. No.	PEROXIDE	AMOUNT (mole%)	MAH wt.%	INITIAL POLYMER TYPE	MFR	TEMP ('C)	TIME (min.)	GRAFTED Wt.%	MFR	HALF LIFE, $t_{1/2}$ @ 180°C (seconds)*
		REACTANTS				REACTION CONDITIONS		POLYMER PRODUCT		PEROXIDE
1-C	dicumyl peroxide	0.07	5	isoPP*	3.0	180	10	0.2	42	23
2-C	dicumyl peroxide	0.16	5	isoPP	3.0	180	10	0.3	120	23
3-C	dicumyl peroxide	0.24	5	isoPP	3.0	180	10	0.5	130	23
4-C	dicumyl peroxide	0.31	5	isoPP	3.0	180	10	0.4	160	23
5-C	dicumyl peroxide	0.47	5	isoPP	3.0	180	10	0.7	>500	23
6-C	dicumyl peroxide	0.62	5	isoPP	3.0	180	10	0.8	>500	23
7-C	dicumyl peroxide	0.78	5	isoPP	3.0	180	10	1.6	>500	23
8-C	dicumyl peroxide	1.75	10	isoPP	3.0	180	10	1.6	>500	23
9-C	Lupersol 101	1.75	10	isoPP	3.0	180	10	1.6	>500	37
10-C	t-butyl peracetate	1.75	10	isoPP	3.0	180	10	1.1	380	9
11-C	benzoyl peroxide	1.75	10	isoPP	3.0	180	10	1.0	330	3
12	isonanoyl peroxide	1.61	20	isoPP	3.0	210	5	1.9	62	0.5
13	t-butyl per-oxypivalate	1.75	10	isoPP	3.0	180	10	1.6	32	0.25

*isoPP = isotactic polypropylene

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1   Table 2 vividly illustrates that the MFR of the polymers
2   maleated in accordance with the preferred process of this
3   invention using preferred peroxide initiators, such as t-butyl
4   peroxypivalate and isononanoyl peroxide are well below one hundred
5   (100) demonstrating that minimal molecular weight degradation
6   occurs with peroxide initiators which satisfy the criteria set
7   forth for use in this invention, while still grafting significant
8   amounts of maleic anhydride.
9   As illustrated by the contrast of Examples 12 and 13 with
10   Examples 1-11, it is also important to the process of this
11   invention that the peroxide initiators have a relatively short
12   half-life at 180°C. The half-life values identified in Table 2
13   for each peroxide were calculated using activation energies and
14   rate constant data from the Polymer Handbook, 2nd Edition,
15   Brandrup & Immergut. The two preferred peroxide initiators, for
16   example, have a half-life of tenths of a second at 180°C. Once
17   chosen, the peroxide initiators, with a half-life of less than
18   about three seconds at 180°C, can be used at any temperature. A
19   peroxide having a half-life of over a few seconds at 180°C will
20   produce a maleated polypropylene product which has a significantly
21   reduced molecular weight.
22   The following examples Nos. 14-22 illustrate the melt phase
23   mode of maleation of polypropylene in accordance with the process
24   of this invention.
25   Example 14
26   T-butyl peroxypivalate as the peroxide initiator, maleic
27   anhydride, and polypropylene pellets (MFR = 1.0) were added
28   directly to the feed hopper of a single screw extruder-reactor and
29   then passed into the feed zone of the extruder. The polymer
30   passed through all zones of the reactor, held at 180°C, with an
31   average residence time of 1.5 minutes. The amount of peroxide and
32   maleic anhydride used, and the product MFR and MAH grafting level
33   are shown in Table 3.
34   Examples 15-21
35   T-butyl peroxypivalate as the peroxide initiator and maleic
36   anhydride were dissolved in methyl ethylketone at ambient
37   temperature, then mixed with polypropylene granules, MFR 3.0. The

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1   solvent was evaporated leaving the MAH and peroxide on the surface
2   of the polymer. A Brabender plasticorder was brought to a
3   temperature of 180°C and rotated at 30 rpm. While rotating at 30
4   rpm the peroxide-maleic anhydride-polypropylene mixture was added
5   to the Brabender plasticorder after which the speed of the
6   Brabender was increased to 60 rpm. The polymer mixture was
7   blended for 10 minutes at 180°C, then removed from the Brabender.
8   The amount of peroxide and maleic anhydride used and the time of
9   reaction varied and is reported for each example in Table 3 which
10 follows.

11 Example 22

12   The procedure of Example 20 was followed except that the
13 Brabender plasticorder was brought to a reaction temperature of
14 200°C and the peroxide-MAH-polymer mixture was blended for only 2
15 minutes. The results are reported in Table 3.

16   The following examples Nos. 23-25 illustrate the solid phase
17 mode for maleation of polypropylene in accordance with the process
18 of this invention.

19 Examples 23-25

20   Maleic anhydride and t-butyl peroxypivalate (TBPP) as the
21 peroxide initiator were dissolved in methyl ethylketone at ambient
22 temperature, then mixed with polypropylene granules, MFR 3.0. The
23 solvent was evaporated leaving the MAH and peroxide on the surface
24 and in the pores of the polymer granules. The dry mixture of
25 peroxide-MAH-polypropylene was added to an autoclave and the
26 autoclave was purged with nitrogen for 15 minutes. The autoclave
27 was evacuated to 10^{-3} torr and then closed to external
28 atmosphere. The autoclave was then heated to 150°C and stirred
29 for a period of time after which its temperature was reduced to
30 room temperature and it was returned to atmospheric pressure.
31 The amount of peroxide and maleic anhydride used and the
32 temperature and time of reaction for each example are summarized
33 in Table 3.

Table 3.

EXP. No.	PEROXIDE	AMOUNT (mole%)	MAH wt%	INITIAL POLYMER TYPE	MFR	TEMP (°C)	TIME (min.)	GRAFTED Wt%	MFR
		REACTANTS				REACTION CONDITIONS		POLYMER PRODUCT	
14	TBPP**	0.21	1	isoPP*	1.0	180	1.5	0.3	6
15	TBPP	0.89	5	isoPP	3.0	180	10	0.7	33
16	TBPP	1.75	10	isoPP	3.0	180	10	1.2	28
17	TBPP	4.40	25	isoPP	3.0	180	10	1.9	35
18	TBPP	5.30	30	isoPP	3.0	180	20	2.3	42
19	TBPP	0.89	5	isoPP	3.0	180	10	0.7	30
20	TBPP	2.67	15	isoPP	3.0	180	10	1.2	36
21	TBPP	4.42	25	isoPP	3.0	180	10	1.9	35
18	TBPP	4.42	25	isoPP	3.0	180	20	2.3	42
22	TBPP	2.67	15	isoPP	3.0	200	2	1.2	59
23	TBPP	2.67	30	isoPP	3.0	150	60	0.5	1.8
24	TBPP	2.67	20	isoPP	3.0	150	180	1.1	3.2
25	TBPP	2.67	20	isoPP	3.0	150	300	1.4	0.9

* IsoPP - isotactic polypropylene

** TBPP - t-butyl peroxpivalate

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1   Table 3 demonstrates that parameters such as temperature,
2 reaction time, apparatus type, and reagent concentration can be
3 varied to control the level of grafting and molecular weight
4 breakdown during PP functionalization. In particular it should be
5 noted that when an enclosed apparatus such as an extruder is used
6. (Example 14) a much lower quantity of reagents is required to
7 obtain similar grafting results to the Brabender, which is open at
8 the top.
9   The polymers useful in this invention include polypropylene
10 and random or block copolymers of propylene with a lesser amount
11 of one or more (C_2-C_{18}) α-olefins and/or diolefins such as
12 ethylene, butene, hexene, butadiene, hexadiene, and so on. Use of
13 such copolymers results in even higher grafting levels and lower
14 MFR levels than are achieved in the case of homopolypropylene.
15 The lower MFR is achieved because, in addition to the elimination
16 of molecular weight breakdown as described by this invention, some
17 crosslinking occurs in the presence of a peroxide in a copolymer
18 containing other olefins, such as ethylene. This crosslinking
19 phenomenon is well known in the art. Example Nos. 26-32
20 illustrate the application of this invention to copolymers of
21 propylene with ethylene. The results of such examples are shown
22 in Table 4.
23   Examples 26 through 29 illustrate melt phase maleation of
24 ethylene-propylene copolymers using the process of this
25 invention. Example 30 illustrates melt phase maleation of
26 ethylene-propylene using prior art. The results are summarized in
27 Table 4.
28 Example 26
29   An ethylene-propylene copolymer containing 3 weight percent
30 ethylene was maleated in accordance with the process of the
31 invention. Maleic anhydride and t-butyl peroxypivalate (TBPP) as
32 the peroxide initiator were dissolved in methyl ethylketone or
33 pentane at ambient temperature, then mixed with polypropylene
34 granules, MFR 3.0. The solvent was evaporated leaving the MAH and
35 peroxide on the surface and in the pores of the polymer granules.
36 A Brabender plasticorder was brought to a temperature of 180°C and
37 rotated at 30 rpm. While rotating at 30 rpm the peroxide-maleic

1   anhydride-polypropylene mixture was added to the Brabender

2   plasticorder after which the speed of the Brabender was increased

3   to 60 rpm. The polymer mixture was blended for 10 minutes at

4   180°C, then removed from the Brabender.

5   Example 27

6   The procedure of Example 26 was followed except that the

7   ethylene-propylene copolymer used contained 5 weight percent

8   ethylene.

9   Example 28

10   The process and procedure of Example 14 (extruder reactor) was

11   followed except that the polymer used was an ethylene-propylene

12   copolymer.

13   Example 29

14   The process and procedure of Example 28 was followed except

15   that the temperatures in the last 2 segments of the extruder were

16   raised to 200°C and 220°C respectively.

17   Example 30-C

18   The process and procedure of Example 14 (extruder reactor) was

19   followed except that the polymer used was an ethylene-propylene

20   copolymer and the peroxide used was a 2,5-dimethyl-2,5-di

21   (t-butylperoxy)hexene (tradename Lupersol 130). The results are

22   summarized in Table 4.

23   Examples 31 and 32 illustrate the solid phase maleation of

24   ethylene-propylene copolymers using the process of this invention.

25   Example 31

26   An ethylene-propylene copolymer containing 3 weight percent

27   ethylene was maleated in accordance with the process of the

28   invention. Maleic anhydride and t-butyl peroxypivalate as the

29   peroxide initiator were dissolved in methyl ethylketone or pentane

30   at ambient temperature, then mixed with polypropylene granules,

31   MFR 3.0. The solvent was evaporated leaving the MAH and peroxide

32   on the surface and in the pores of the polymer granules. The dry

33   mixture of peroxide-MAH-polypropylene was added to an autoclave

34   and the autoclave was purged with nitrogen for 15 minutes. The

35   autoclave was evacuated to 10^{-3} Torr and then heated to 150°C.

36   The contents were stirred for 60 minutes.

37   Example 32

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Table 4.

EXP. No.	REACTANTS				INITIAL POLYMER		REACTION CONDITIONS		POLYMER PRODUCT	
	PEROXIDE	AMOUNT (mole%)	MAH wt.%		TYPE	MFR	TEMP (°C)	TIME (min.)	GRAFTED Wt.%	MFR
20	TBPP**	2.67	15		isoPP*	3.0	180	10	1.2	36
26	TBPP	2.67	15		3% ethylene copolymer of PP	3.0	180	10	1.4	35
27	TBPP	2.67	15		5% ethylene copolymer of PP	3.0	180	10	2.0	23
28	TBPP	0.21	1		1.5% ethylene copolymer of PP	1.7	180	1.5	0.44	6
29	TBPP	0.21	1		1.5% ethylene copolymer of PP	1.7	180-220	1.5	0.44	6
30-C	TBPP	0.21	1		1.5% ethylene copolymer of PP	1.7	180	2.5	0.49	540
23	TBPP	2.67	30		isoPP	3.0	150	60	0.50	1.8
31	TBPP	2.67	30		3% ethylene copolymer of PP	3.0	150	60	0.80	4
32	TBPP	2.67	30		5% ethylene copolymer of PP	3.0	150	60	1.7	0.5

* isoPP = isotactic polypropyslene
** TBPP = t-butyl peroxypivalate

1   The procedure of Example 26 was followed except that the
2   ethylene-propylene copolymer used contained 5 weight percent
3   ethylene. The results are summarized in Table 4.
4   Examples 31 and 32, conducted at 150°C show that significantly
5   less molecular weight degradation occurs in the solid phase
6   experiment than in the melt phase experiment. Comparison of
7   Examples 26-28 with the previous examples demonstrates that the
8   crosslinking affect achieved with the presence of ethylene
9   monomeric units in the polypropylene polymer results in slightly
10   lower MFR than when the crosslinking ability is not present
11   (homopolypropylene). Concomitantly, the 5 percent ethylene
12   copolymer exhibits the lowest MFR under the same maleation
13   conditions.
14   The foregoing disclosure and description of the invention are
15   illustrative and explanatory thereof, and various changes in the
16   size, shape and materials, as well as in the details of the
17   illustrated construction may be made without departing from the
18   spirit of the invention.

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CLAIMS:

1. A functionalized (co)polypropylene comprising:
    polypropylene having more than 0.13 mole percent
    grafted functional groups derived from substituted
    vinyl monomers that are capable of free radical
    polymerization, said functionalized polypropylene
    having an MFR of 100 or less.

2. The functionalized polypropylene of claim 1 wherein the
    vinyl monomer is one of an unsaturated acid, anhydride,
    amide, ester, or a siloxane.

3. The functionalized polypropylene of claim 1 having more
    than 0.17 mole percent grafted functional groups.

4. The functionalized polypropylene of claim 2 wherein the
    grafted functional groups are derived from maleic
    anhydride, himic anhydride, acrylic acid, methacrylic
    acid, vinyltrimethoxysilane, acrylamide, itaconic acid,
    maleic acid, fumaric acid, monomethyl maleate, monoethyl
    maleate, fumaric anhydride, vinyl amines and amides.

5. The functionalized polypropylene of claim 2 wherein the
    grafted functional groups are derived from an unsaturated
    anhydride.

6. The functionalized polypropylene of claim 5 wherein the
    anhydride is maleic anhydride.

7. The functionalized polypropylene of claim 6 having
    0.13 - 1.71 mole percent grafted maleic anhydride.

8. The functionalized polypropylene of claim 1 derived from
    homopolypropylene.

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9. The functionalized polypropylene of claim 2 derived from a ,
    copolymer or terpolymer of propylene with a lesser amount of one
    or more of a C_2-C_{18} α-olefin or diolefin.

10. A free radical process for functionalizing polypropylene,
    comprising:
    adding to polypropylene an unsaturated
    functionalizing agent and a free radical initiator
    wherein;
    said unsaturated functionalizing agent is an acid,
    anhydride, amide or a siloxane; and
    said free radical initiator is a peroxide producing
    radical fragments, selected from the group
    consisting of R• and RO•, where R is a
    C_1 - C_{30} aliphatic hydrocarbon and O is oxygen;
    and
    heating the polypropylene while in contact with said
    free radical initiator and said functionalizing
    agent at a temperature sufficient to graft the
    functionalizing agent to the polypropylene, whereby
    the polypropylene is functionalized with minimal
    molecular weight degradation.

11. The process of claim 10, wherein:
    the initiator is a peroxide having a $t_{1/2}$ of less
    than three seconds at 180°C.

12. The process of claim 11, wherein:
    R is *t*-butyl when the radical fragment is RO•.

13. The process of claim 12, wherein:
    the peroxide initiator is isononanoyl peroxide.

14. The process of claim 11, wherein:
    the peroxide initiator upon dissociation has one
    radical fragment with an alkoxy group, and another
    radical fragment with an alkyl group.

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15. The process of claim 14, wherein:
    the peroxide initiator is t-butyl peroxypivalate.

16. The process of claims 13, 14 or 15, wherein:
    the functionalizing agent is maleic anhydride.

17. The process of claim 16, wherein:
    the polypropylene is heated to a temperature
    sufficient to melt the polypropylene so that the
    polypropylene is in the melt phase during the
    grafting reaction of the maleic anhydride to the
    polypropylene chain.

18. The process of claim 16, wherein:
    the polypropylene is heated to temperature
    insufficient to melt the polypropylene so that the
    polypropylene is in the solid phase during the
    grafting reaction of the maleic anhydride to the
    polypropylene chain.

19. The process of claim 16, wherein:
    the polypropylene is first heated, and the maleic
    anhydride and peroxide are added.

20. The process of claim 17, wherein:
    the temperature in the melt phase is from about the
    melt temperature of the polypropylene to about 250°C.

21. The process of claim 10, wherein:
    the amount of initiator present in the reaction with
    the polypropylene is equivalent to between about 0.14
    mole percent and 6 mole percent based on the number
    of moles of monomer present.

22. The process of claim 10, wherein:
    the resulting functionalized polypropylene has a melt
    flow rate of about one hundred (100) or less.

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23. The process of claim 10, wherein:
    the resulting functionalized polypropylene has an
    average of two or more functional groups for each
    polypropylene chain.

24. The product produced by the process of claim 10.

25. The product produced by the process of claim 12.

26. The product produced by the process of claim 21.

27. The product produced by the process of claim 22.

28. The product produced by the process of claim 23.

Figure 1

Melt Flow Rate vs. Wt.% Grafted MAH

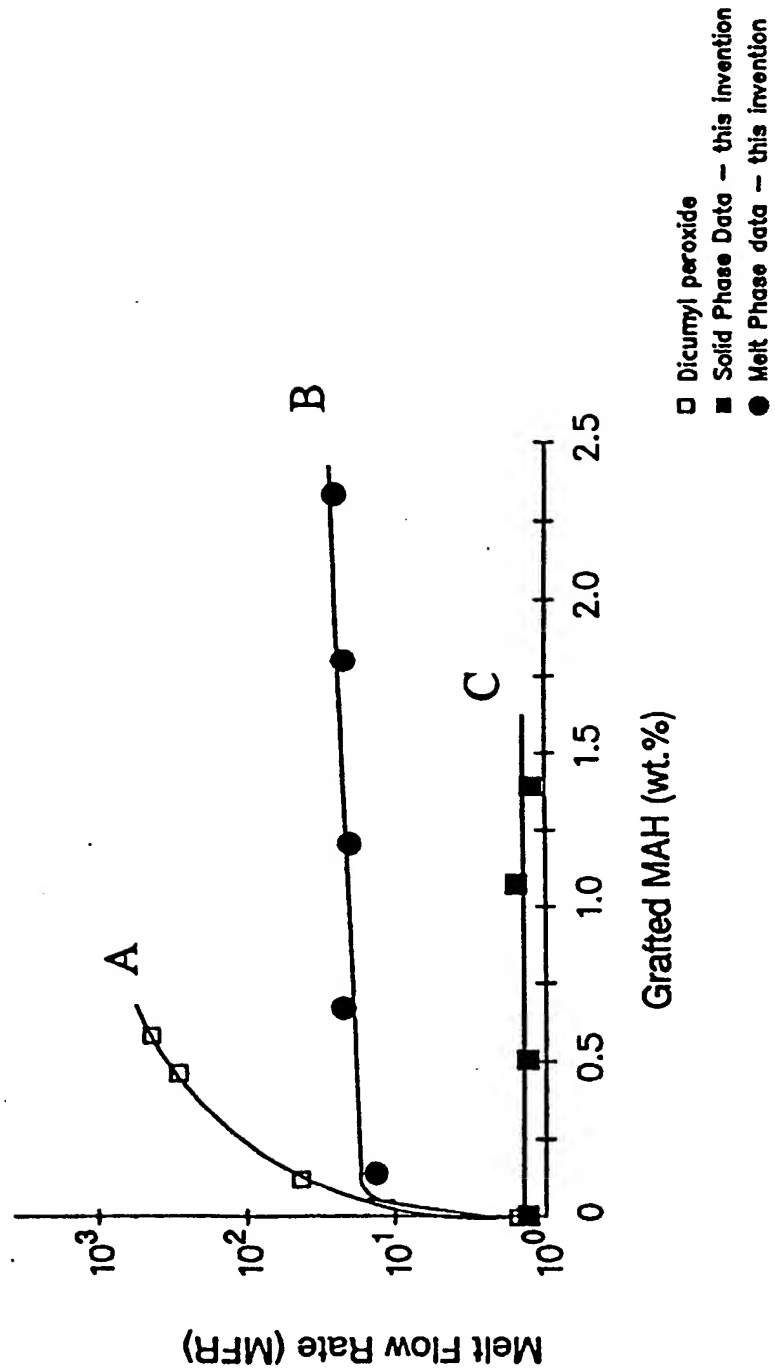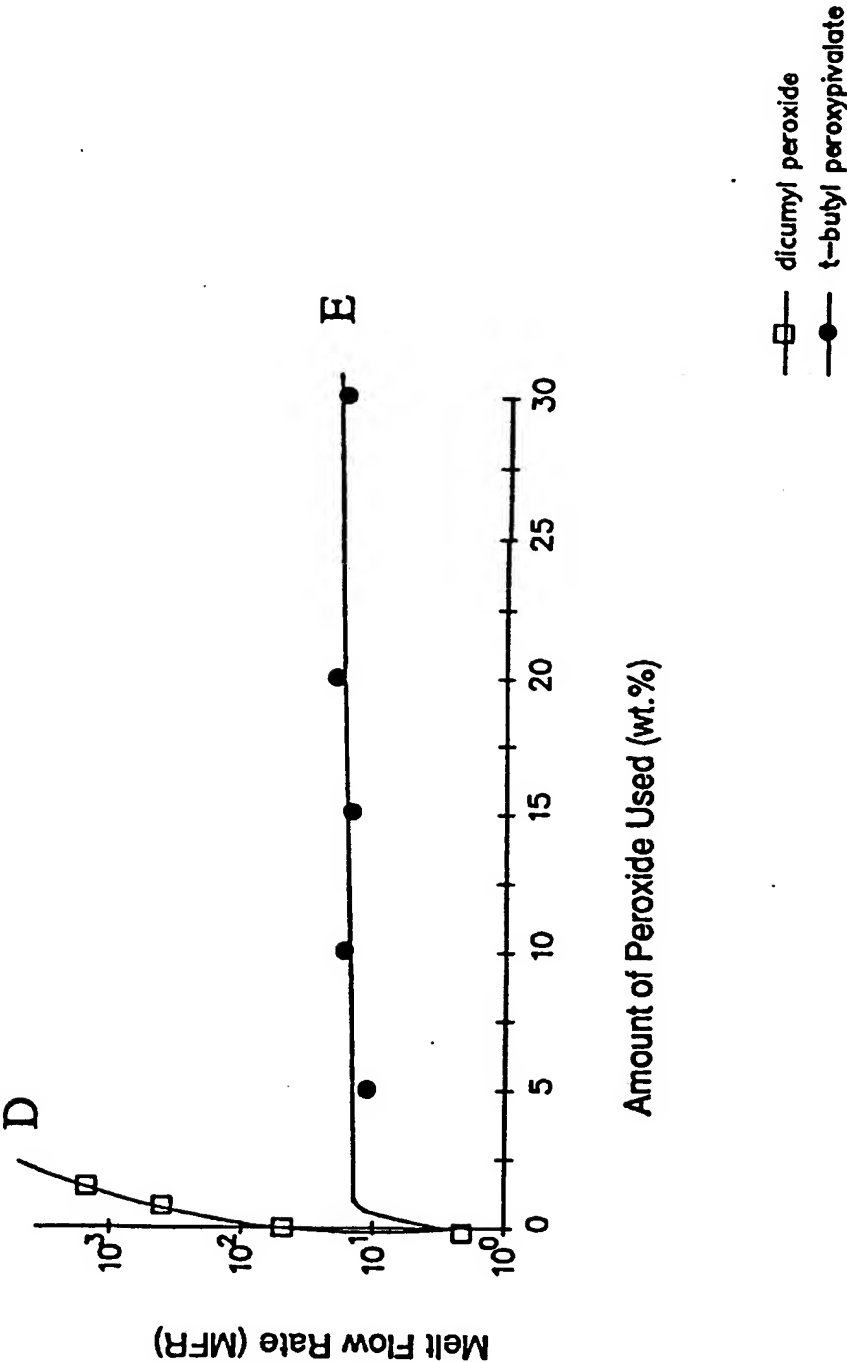during grafting of Homopolypropylene

□ Dicumyl peroxide
■ Solid Phase Data — this invention
● Melt Phase data — this invention

Figure 2

The Effect of Peroxide on Melt Flow Rate
during grafting of Homopolypropylene

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: C 08 F 255/00, C 08 F 8/46

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷	
Classification System	Classification Symbols
IPC⁵	C 08 F

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP, A, 0134941 (DYNAMIT NOBEL) 27 March 1985 see claims 1-7	1-28
Y	FR, A, 2186490 (EASTMAN KODAK) 11 January 1974 see claims 1-8	1-28
Y	US, A, 4506056 (N.G. GAYLORD) 19 March 1985 see claim 1; column 4 (cited in the application)	1-28
A	FR, A, 2251611 (EASTMAN KODAK) 13 June 1975 see claims 1-4	1
	./.	

* Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
9th August 1990	17. 09. 90
International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	M. SOTELO

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages	Relevant to Claim No.
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A	EP, A, 0082704 (E.I. DU PONT DE NEMOURS) 29 June 1983 see claims 1-4. & US, A, 4639495 (cited in the application) --	1
A	FR, A, 1482380 (HERCULES POWDER) 26 May 1967 see summary; page 2, column 1 & US, A, 3414551 (cited in the application)	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 9002189
SA 37026

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 07/09/90
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		NL-A-	6607411	27-12-66
		US-A-	3414551	

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